

Removal of Sulphur Dioxide by Zeolite Synthesized from Fly Ash and Alkali Hydroxide

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in Partial Fulfillment of the Requirements
for the Degree of**

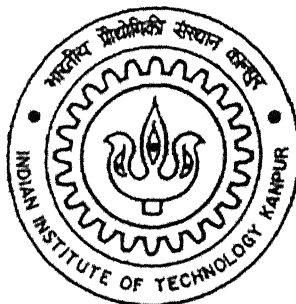
MASTER OF TECHNOLOGY

in

Environmental Engineering and Management

by

SANDEEP SHRIVASTAVA



To the

**DEPARTMENT OF CIVIL ENGINEERING
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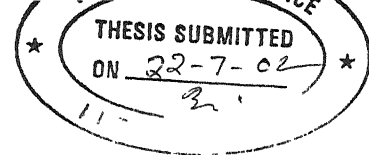
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Dedicated
To
Papa, Mummy and Didi



CERTIFICATE

This is to certify that the work contained in the thesis entitled 'Removal of Sulphur Dioxide by Zeolite Synthesized from Fly Ash and Alkali Hydroxide', by Sandeep Shrivastava, has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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ABSTRACT

In the present work, removal of sulphur dioxide by the zeolite, synthesized from fly ash and alkali hydroxide was studied. Synthesis of zeolite was done at different temperatures by treating fly ash with different concentrations of alkali hydroxide. Physical properties of different zeolites were also examined to choose suitable zeolite for removal of sulphur dioxide. Fly ash treated with 3M sodium hydroxide at 150 °C showed zeolitization and formation of sodium zeolite with average pore diameter 6.3 Å and fly ash treated with 3M monohydrous lithium hydroxide at 90 °C showed zeolitization and formation of lithium zeolite with average pore diameter 7.8 Å.

The feed gas containing 2500 ppm of sulphur dioxide was passed through the bed of zeolite dispersed in sand at 25 °C and 2037 hr⁻¹ space velocity. Under this condition synthesized Na-Zeolite and Li-Zeolite removed 63 % and 74.3 % of sulphur dioxide, respectively. Breakthrough curves for sulphur dioxide at different temperatures and different inlet concentrations were also generated to study the effect of operating temperature and inlet sulphur dioxide concentration on removal of sulphur dioxide. Regeneration was possible in the case of Li-Zeolite at the temperature 650 °C in the absence of Oxygen. However, removal efficiency was reduced to 42 % after the third cycle. On the basis of above study it is clear that zeolite synthesized from fly ash and alkali hydroxide may be used to remove sulphur dioxide and synthesized Li-Zeolite has better sulphur dioxide removal efficiency than synthesized Na-Zeolite.

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1. Introduction

Sulphur dioxide is emitted from coal-fired power plants, industrial fuel combustion, and sulphuric acid plants and smelting of sulphur containing ores. The amount of sulphur dioxide discharged at specific place is a function of the sulphur content of the coal used. In India the sulphur content can vary from less than 1% to more than 4% and bituminous type used in power plants has sulphur ($>2\%$)(Survey of Indian Environment, 2000). Sub-bituminous coal, lignite, and anthracite have low sulphur content ($<1\%$), unfortunately, most low sulphur coal is not burned in power plants because it has a low heating value (Survey of Indian Environment, 2000).

Installation of scrubber and/or use of low sulphur containing coal are two options currently used by utilities to reduce their sulphur dioxide emissions. At this point in time, majorities of utility control their sulphur dioxide emissions using lime based scrubbing. Wet desulphurization process has a number of advantages but it has two major disadvantages, In short term purchase, processing, and landfill disposal costs, associated with lime based scrubbing add approximately 4% to the price of the electricity generated at the plant (A.srinivasan, 1999). As regulations become more stringent this cost will increase. Perhaps less obvious but far more significant is the fact that the use of larger amounts of lime based materials to remove even more sulphur dioxide from flue gases will add increasingly large amount of CO_2 to atmosphere, clearly utilities are in very difficult position. So more economical and effective methods

should be developed to remove sulphur dioxide. Generally removal of sulphur dioxide is carried out by wet scrubbing, this requires considerable equipment, involving high capital and operating cost to complete the process, this laid the dry scrubbing as low cost operation without generating huge amount of liquid waste to dispose. Most of the recent research and development in the area of desulphurization has been focused on development of these dry process as removal of sulphur dioxide was found to be 70-90 % at 15 –30 % less cost than wet process (Dullien, F.A., 1989).

In the present laboratory work, waste product fly ash, and alkali hydroxides were used to synthesize a medium (zeolite) for removal of sulphur dioxide gas. Various zeolites were examined to choose suitable one for removal of sulphur dioxide.

2. Background Information

An important reason for controlling air pollutants such as sulphur dioxide is the damaging effects they have on human health. These effects include premature death, as well as increase in the incidence of chronic heart and lung disease. Sulphur dioxide has received major attention for many years in the group of irritant anthropogenic air pollutants, they are widely prevalent and of unquestioned physiological significance at higher concentrations. The major health concerns associated with exposure to high concentrations of sulphur dioxide include breathing difficulties, respiratory illness, and aggravation of existing cardiovascular disease. In addition to the health impacts, sulphur dioxide leads to acid deposition in the environment. This deposition causes acidification of lakes and streams and damage to tree foliage and agricultural crops. Furthermore, acid deposition accelerates the decay of buildings and monuments. While airborne, sulphur dioxide and its particulate matter derivatives contribute visibility degradation (Wark, and Warner, 1981).

Electric power generation units account for the majority of sulphur dioxide emissions. These units contribute more than half of percent of the national sulphur dioxide emissions (Survey of Indian Environment, 2000). Power generating units may use flue gas desulphurization technologies. Additionally, the use of these technologies can result in the reduction of fine particle precursor emissions and mercury emissions from combustion units. It is timely, therefore, to examine the current status of sulphur dioxide removing technologies.

2.1 Sources of Sulphur Dioxide

Sulphur is an element present in all natural mineral oils and coal with a composition varying from less than one to over four percent (Nriagu, 1978). Thus the total emission of sulphur dioxide varies considerably with the nature or the origin of fossil fuel. During the combustion of these fossil fuels, most of the sulphur is oxidized to sulphur dioxide and sulphur trioxide. About 99 percent of the total sulphur is emitted as sulphur dioxide and 0.2 to 1.0 percent as sulphur trioxide (Stern, 1977). The sources of the oxides of sulphur are natural as well as anthropogenic, the latter being of prime importance to a pollution control engineer. The natural sources contributing to sulphur dioxide pollution are forest fires, volcanic eruptions and conversion of hydrogen sulphide into sulphur dioxide in the atmosphere (Nriagu, 1978).

2.2 Effects of Sulphur Dioxide on the Environment

2.2.1 Effects on Vegetation

Different species and variety of plants vary in their sensitivity to sulphur dioxide exposure. Alfalfa is most sensitive species with acute injury observed at a dose of 1 ppm for 1 hour (Godish, 1985). Sulphur dioxide enters into stomata of leaves and immediately comes in contact with spongy mesophyll cells in the vicinity of the pores, where the toxic response was initially manifested and with time there is progressive expansion of injury and tissue collapse. The injury caused to leaf by sulphur dioxide

may lead to plant damage and loss of crop yield. Table 2.1 shows the sensitivity of plants to various pollutant gases.

Table 2.1 Sensitivity of plants to pollutant gases (Times of India, 14 Feb.2001)

Ozone Sensitive	Carnation, Petunia, Lilac and Marigold
Sulphur Dioxide Sensitive	Aster, Canna, Zinnia, Sweet Pea
Fluoride Sensitive	Tulip, Gladiolus, Phlox, Daisey
Nitrogen Dioxide Sensitive	Azalea, Balsam, Dahlia
PAN Sensitive	Dahlia, Petunia and Rose
Ethylene Sensitive	Carnation, Marigold and Rose

2.2.2 Effects on Human Health

Various animal Species, including man respond to sulphur dioxide by bronchoconstruction that may be assessed in terms of a light increase in airway resistance. Sulphuric acid is much more potent irritant to man than is sulphur dioxide; therefore, most studies deal with combined sulphurous materials rather than with sulphur dioxide alone. Typical concentration data and associated health effects are presented in the table 2.2.

Table 2.2 Health effects of sulphur dioxide (Stern et al, 1984)

Concentration (ppm)	Exposure Time (min)	Health Effects
0.5	10	airways resistance in asthmatics at exercise
5	10	Increased airway resistance in asthmatics at rest
8	-	Throat irritation in healthy adults
10	10	Bronchospasm
15	60	Decreased mucociliary activity
20	-	Eye irritant, Coughing in adults
400	-	Lung edema, Bronchial inflammation

2.2.3 Acid Rain

Acid rain has been developed into one of the most intractable air pollution problems in temperate regions. It was primarily linked to the drastic increase in global sulphur dioxide emissions. Acid deposition has a considerable impact not only on surface water, but also on soils and ground water, mobilizing micronutrients and heavy metals and thereby impoverishing the status of the soils and poisoning drinking water.

(Acid Rain – Another Disaster in the Making, Homepage of Tata Energy Research)

2.3 Sulphur Dioxide Control Technologies

Various technologies exist that have been designed to remove sulphur dioxide from flue gas produced by various plants. These technologies represent a varying degree of commercial readiness. Some can claim tens of thousand of hours of operational

experience, while others have only recently been demonstrated at commercial plants. Commercially available desulphurization technologies can “conventionally” be classified as once through and regenerable, depending on how sorbent was treated after it has sorbed sulphur dioxide. In once-through technologies, the sulphur dioxide is permanently bound by the sorbent, which must be disposed of as a waste or utilized as a by-product (e.g., gypsum). In regenerable technologies, the sulphur dioxide is released from the sorbent during the regeneration step and may be further processed to yield sulphuric acid, elemental sulphur, or liquid sulphur dioxide. The regenerated sorbent is recycled in the sulphur dioxide scrubbing step. Both once-through and regenerable technologies can be further classified as wet or dry. In wet processes, wet slurry waste or by-product is produced, and gas leaving the absorber is saturated with moisture. In dry processes, dry waste material is produced and gas leaving the absorber is not saturated with moisture. Depending on process configuration and local market conditions at the plant site, once through wet Desulphurization processes can produce slurry waste or salable by-product. This waste/by-product must be dewatered in some fashion prior to disposal or sale (in case of a salable by-product). The “conventional” classification of desulphurization processes is shown in table 2.3. The general objective of the desulphurization process is to convert the sulphur to a compound other than sulphur dioxide that is simpler to separate from the flue gas. The sorption processes, or preferential sorption of sulphur dioxide by liquid and solid materials to form sulphites or sulphates in a liquid or solid form, are the most common removal methods. Oxidation of sulphur dioxide to SO_3 in the gas stream and further condensation of sulphuric acid is the second most popular method.

Table 2.3 Desulphurization processes

Through away		Regenerative	
Wet	Dry	Wet	Dry
Limestone Forced Oxidation	Lime Spray Drying	Magnesium oxide	Activated Carbon
Limestone Inhibited Oxidation	Duct Sorbent Injection	Sodium Carbonate	
Lime	Furnace Sorbent Injection	Amine	
Magnesium Enhanced Lime Seawater	Circulating Fluidized Bed		

1 Throw away and Regenerative Process

The throw away process forms a product intended to be disposed entirely as waste. The removal of sulphur dioxide is mainly done by calcium-based (limestone, lime) sorbents, which have high sulphur dioxide sorption ability. Conventional processes included in this category are the limestone/sludge and lime/sludge. The throwaway methods have the disadvantage that the contamination problem is not completely solved; but just transferred from gaseous to solid phase.

The regenerative processes regenerate the original reactants and concentrate the sulphur dioxide that is removed from the flue gases. The concentrated sulphur dioxide can be chemically transformed into sulphuric acid or elemental sulphur, or physically condensed into liquefied sulphur dioxide (Satriana, 1981). The carbon adsorption, the ZnO, and the copper oxide processes are included in this category. The interest in

these processes was due to the regeneration of the sorbent, the production of a saleable product, and the fact that there is no waste generated.

2.3.2 Dry and Wet Process

Both the throwaway and the regenerative processes can be either dry or wet. Dry process involves contacting flue gas with an alkaline material to remove the sulphur dioxide and generates a dry waste product, while wet scrubbing involves the use of a liquid phase for removing of impurities. The main advantage of the dry systems over the wet systems is that they have less energy requirements due to savings in reheating and pumping the stack gas. Since the stack gas is not cooled during the removal of sulphur dioxide, it has the same thermal buoyancy leaving the stack that it has during normal operation.

There are also several disadvantages with the dry systems (Dullien, 1989; Slack and Hollinden, 1975; Satriana, 1981). One of them was the higher cost of materials. The reagents used in dry systems are more expensive than those used in wet systems, and a high stoichiometric ratio of sorbent to entering sulphur dioxide is needed, since the sorbent utilization per pass is lower per unit of active sorbent than in a wet system. Furthermore, the regenerated particles suffer from inactivation and physical attrition after several cycles of sorption and regeneration, in fluidized and moving beds.

Wet scrubbing is the most important air pollution control process used in industrial practice, in terms of cost and sheer volume systems (Dullien, 1989; Slack and Hollinden, 1975; Toole-O'Neil, 1998). Compared with the dry systems, the wet systems

offer the advantages that physical deterioration of the sorbent was less likely to occur and mass transfer was larger in the liquid phase. But in wet systems, non-desired chemical reactions are more suitable to occur, and there are expenses included in separating water from the product, both for regeneration in recovery processes and for discard in throw away methods. The reheat of the gas before release is another factor to be considered in the economics.

2.3.3 Current Technology

More recently, Chriswell and Gollakota (1987), and Gollakota and Chriswell (1988) published papers that showed that the use of acid resistant Silicalite would give zero release and adsorb ~58 mg sulphur dioxide per gram of zeolite at 25°C from a simulated coal burning flue gas. The technology worked very well, the work accomplished by synthesizing its own zeolites from fly ash and then using the zeolites to remove sulphur dioxide. The project has been successful. However, removal efficiencies are about 1/6th that of Silicate (10 mg solid), but the fly ash samples are only partially converted and still contain a significant amount of unreacted fly ash. Work is continuing to increase reactivities using more alkaline solutions, ball milling of the fly ash, and zeolite seeds.

It is known that sulphur dioxide may be adsorbed on a molecular sieve quite efficiently (Chriswell, c; Golacota, 1987). It is also known that use of commercial silicate zeolite is not cost-effective and zeolites are found in nature but the formation process is very slow (Amrhein, C., Haghnia, G. H., 1996), it may take hundreds of years to get natural zeolites. During this process volcanic ashes are converted to zeolite by the

action of alkaline /saline surface and /or ground water on deposits of glassy ashes (Breck, D.W., 1973). Zeolite formation from fly ash and alkali hydroxide has been successfully carried by Srinivasan et.al (Srinivasan, A., 1999) and Larosa et.al (LaRosa, J; s. Grutzeck, 1992).

Much of the interest in aluminosilicate adsorbents depends upon the arrangement and free dimensions of the intra crystalline channel structure. This can be measured as water volume or one may take framework as density or openness the No. of (Al+Si) atoms per 1000 \AA . This leads to a correlation, which does not take the form of a line but band with approximate upper and lower envelopes (Barrer R.M, 1982). This suggested that the adsorption capacity is not only dependent of frame density but also the distribution of pores and their accessibility and also on the cation, which can vary in size, valance and No (Barrer R.M, 1982). As lithium has less atomic size so it may be possible that fly ash treated with lithium hydroxide will have more surface area and will remove sulphur dioxide more effectively. It is predicted that Li-Zeolite will result in larger pore diameter and larger surface area, which may enhance the removal of sulphur dioxide. But cost of $\text{LiOH}\cdot\text{H}_2\text{O}$ is much more than that of NaOH so it should be tried to synthesize and analyze Li-Zeolite at the low temperature.

On the basis of above information in the present experimental work various lithium and sodium zeolites were synthesized from fly ash and alkali hydroxide and were examined to choose suitable zeolite for removal of sulphur dioxide.

3. Scope of Present work

On the basis of background information it is clear that zeolite may be used as medium for removal of sulphur dioxide, but in nature formation of zeolite takes hundreds of years and commercial zeolites are costly to use for removal of sulphur dioxide (LaRosa, J., S.Grutzeck, 1992).

The present work deals with the synthesis of zeolite from waste product fly ash and alkali hydroxide to study the removal of sulphur dioxide by synthesized zeolite in a packed bed reactor of zeolite dispersed in sand. Background information also indicates the possibility of more pore diameter and porosity in the case of zeolite synthesized from fly ash and lithium hydroxide than that of zeolite synthesized from fly ash and sodium hydroxide. Therefore, objectives of this work may be stated as following:

1. To find out the conditions of zeolite formation to get suitable zeolite for removal of sulphur dioxide.
2. To generate breakthrough curves for sulphur dioxide in packed bed of zeolite dispersed in sand under various conditions of temperature and inlet sulphur dioxide concentration.
3. To study whether synthesized Li-Zeolite is more effective in removal of sulphur dioxide than synthesized Na-Zeolite and to study the regeneration of zeolite.

It is expected that the experimental study will throw light on the use of synthesized zeolite as sulphur dioxide removal medium under the various process and conditions stated above.

4. Materials and Methods

4.1 Fly Ash

Aluminosilicates are the major mineral compounds present in fly ash. Other crystalline minerals include quartz, mullite, hematite, lime, and feldspars. These chemical and mineralogical features make fly ash a strong candidate for zeolitization. SiO_2 and Al_2O_3 were the major components and the most important reagents for treatment. Other crystalline phases identified included mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), quartz (SiO_2), hematite (Fe_2O_3), and lime (CaO). Low carbon fly ash may be readily treated to form aluminosilicates. (LaRosa, J., and Kwan, 1992). In the present study fly ash was taken from locally situated Panki thermal power plant. Table 4.1 shows the percentage composition of fly ash.

Table 4.1 Composition of fly ash (Data taken from Panki Power Plant-Kanpur)

Ingredients	Percentage Composition
SiO_2	55.07
Al_2O_3	29.44
Fe_2O_3	2.73
Na_2O	1.73
CaO	1.42
MgO	0.97
K_2O	0.94
P_2O_5	0.24

4.2 Treatment of Fly ash

Fly ash (composition shown in table 4.1) was treated with alkali hydroxide solution in a closed system of teflon reactor. Teflon reactors were used to avoid the reactions of alkali with the silicates present in glass vessels. Typically 100g of fly ash was mixed with different molar concentrations of alkali hydroxide (1.0 M, 2.0 M, 3.0 M) and heated very slowly to different temperatures in a platinum crucible. Mixture was cooled and taken out of furnace. At ambient temperature 10 % (by wt.) of fused fly ash was taken and added to 100 ml of deionized water in a closed teflon reactor and agitated for 24 hours at room temperature. After aging of solution the teflon reactor was sealed and heated to 100⁰ C without stirring for 48 hours. The precipitates were filtered, washed repeatedly with deionized water and dried overnight at 105⁰ C. (Srinivasan and Grutzeck, 1999)

The fly ash so treated was examined with respect to following

4.2.1 BET Surface Area

The specific surface area of fused fly ash was determined by BET surface area analyzer (Model No SA-3100, Coulter Company, England). The surface area was determined by following relation. $S = V_m \cdot A(N/M)$

In this relation V_m was the volume of gas at STP required to form an adsorbed molecular layer, A was the Avagadro's No which expressed the No of gases molecules present per mole of the gas at the standard conditions of temperature and pressure, M

was the molar Volume of gas and N was the area of each adsorbed gas molecule. Measurement of surface area was done by passing the carrier gas in the ratio of 30 % N_2 and 70 % He through the sample. The Nitrogen was used as the adsorbate gas and the helium as carrier gas. The sample holder was immersed in the liquid N_2 bath at a very low temperature (-197°C) at which Nitrogen gas was condensed and was adsorbed onto the surface of adsorbent. The above instrument uses the readymade software, which did all calculations and reported the BET surface area of treated fly ash.

4.2.2 X-Ray Diffraction

Powder XRD analysis was employed to monitor crystals formation process using X-Ray powder diffractometer, which used $\text{Cu-K}\alpha$ as source of X-Ray (Model Isodevyeflux, made by Rich Seifert & Co, West Germany). During all XRD analysis, the X-Ray wavelength was kept constant at 1.540 \AA and the relative intensity of the diffraction was recorded as the function of 2θ . The D-spacing value of standard zeolite sample reported in JCPDS file formed the basis for comparison

4.2.3 Scanning Electron Microscopy (SEM)

The Structural Morphology of fly ash treated with sodium hydroxide and lithium hydroxide was examined by Jeol-840-A, for different temperatures of formation and 3M Concentrations of hydroxides.

4.3 Experimental Set-up

Figure 4.1 represents the schematic diagram of the set-up used in conducting the experiments. The set-up consists of four gas cylinders containing pure gases namely oxygen, carbon dioxide, sulphur dioxide and nitrogen. The gas cylinders mounted with regulators were connected to manometers for measuring the flow. Dibutyl Phthalate containing a pinch of methyl red was used as the manometric liquid. In between the gas cylinders and the manometers needle valves were connected to regulate the flow.

All the gases were allowed to mix in mixing chamber, the mixture of gas thus produced was fed to reactor through the inlet pipe. Reactor properties and operating conditions are shown in table 4.3.

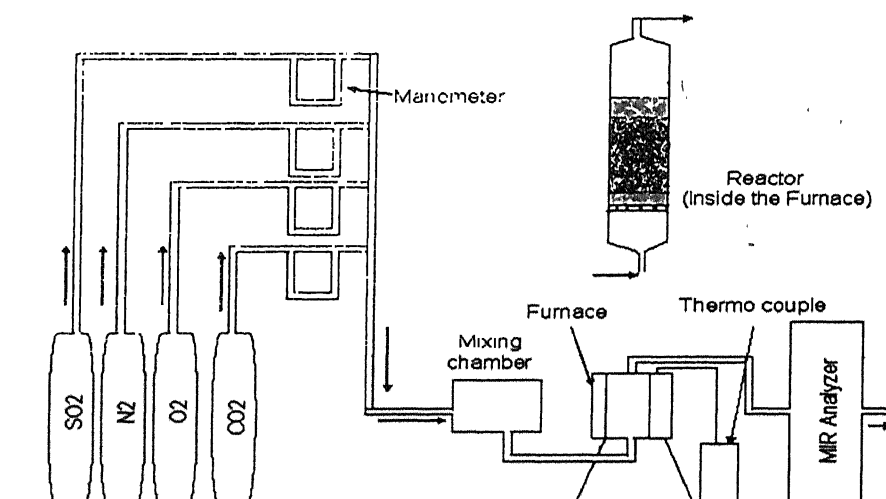


Figure 4.1 Experimental Set-up

Table 4.2 Reactor properties and operating conditions

Sl No.	Particulars	Values
1.	Carrier gas composition (By Volume)	N ₂ ≈85 %, CO ₂ ≈10 %, O ₂ ≈ 5 %, sulphur dioxide= 2500 ppm (± 4 ~5 %)
2.	Operating temperature	Temperature was varied from 25 °C to 200 °C during various experiments.
3.	Concentration of SO ₂ in test gas (ppm)	500 – 2500
4.	Space velocity of test gas (per Hour)	2037
5.	Residence of test gas in reactor (seconds)	1.76
6.	Diameter of bed (mm)	15
7.	Length of bed (mm)	100
8.	Treated fly ash: sand (By weight)	1:10

4.3.1 Experimental Methodology

Laboratory experiments were conducted to investigate the treated fly ash performance on removal of sulphur dioxide. First of all manometers were calibrated to know the actual rate of flow of gases from the cylinders. A feed gas was simulated with appropriate proportion of N₂, O₂ sulphur dioxide and CO₂ and sulphur dioxide. Initially oven dried sand was used as a bed material and when it was exhausted with sulphur dioxide then the same sand was used to mix with fly ash treated with sodium hydroxide and fly ash treated with lithium hydroxide, separately in 1:10 (treated fly ash: sand, by weight) proportion to ensure the pressure loss was within limit of practical field values.

250-300 mm of water (Kohl, A.L., and Riesenfeld, F.C, 1979). Appendix-A reports the pressure loss data of the sand-bed reactor of present study. Now these mixtures were used to check the removal of sulphur dioxide. Break through curves were generated for the same concentration of sulphur dioxide and 25 °C temperatures. Then breakthrough curves were generated for sulphur dioxide at different temperatures (for the same inlet concentration) and for different inlet concentrations of sulphur dioxide (at same temperature). Performance of zeolite dispersed sand bed as plug flow reactor was also verified (Appendix- B).

4.3.2 Calibration of Manometers

Manometers were used in the experimental set up for measuring the flow rate of the component gases. Manometers were calibrated using bubble displacement technique. Manometers were connected to a 50 ml glass burette .The burette had rubber bulb, attached to the bottom of the burette containing soap solution. Soap solution was prepared by mixing some liquid soap in distilled water. The gas was allowed to flow and the difference between the liquid levels between the two limbs of manometers was recorded. The time taken by the soap bubble to travel up the burette was also recorded. The flow of the gas was adjusted so as to obtain 5-6 different sets of readings. Discharge (Q) was plotted against difference in liquid level (ΔH) to obtain a relationship between flow rate and ΔH . This calibration was done for each of the component gases namely oxygen, nitrogen, and carbon dioxide and sulphur dioxide. The different calibration curves are shown in Appendix-C.

4.3.3 Preparation of Feed Gas

The gas mixture was prepared by mixing the individual gaseous constituents from four gas cylinders containing pure gases namely nitrogen, oxygen, carbon dioxide, and sulphur dioxide. The flow of individual gases was controlled and measured with the help of gas regulators and manometers connected with capillary tubes. The individual gas flow was calibrated with the use of a bubble displacement technique. All the four gases were brought to a glass chamber with the help of high-density polyethylene tubes where the gases were mixed to produce a desired mixture of dry flue gas. Concentration of sulphur dioxide was measured with the help of Multigas Infrared Analyzer (MIR 9000, Emission S.A France). Measured concentration was also cross-checked with the concentration, calculated from calibrated manometer. The calculated concentration was found to be within $\pm 4\sim 5\%$ of measured one. Generally the flue gas composition has 76-87 % of N_2 , 8-12 % of CO_2 , 4-8 % of O_2 and trace amounts of pollutant gases like sulphur dioxide (Chu, P., and Rochelle, G.T., 1989). In the present work 10 % of CO_2 , 5 % of O_2 and 2500 ppm ($\pm 4\sim 5\%$) of sulphur dioxide and rest of N_2 were taken to prepare feed gas.

5. Results and Discussions

The experimental data, calculated results, effect of variables on removal of sulphur dioxide and breakthrough curves have been shown in tables and figures of this chapter.

5.1 Analysis of Fly Ash Treated with Alkali Hydroxide

In this section physical properties such as BET surface area, pore diameter and pore volume of fly ash treated with different molar concentrations of alkali hydroxide at different temperatures are presented in table 5.1 for fly ash treated with sodium hydroxide and table 5.2 for fly ash treated with lithium hydroxide.

Table 5.1 Physical properties of fly ash treated with sodium hydroxide

Sl No	Properties	Fly ash + 1M NaOH			Fly ash + 2M NaOH			Fly ash + 3M NaOH		
1.	Flyash:Alkali (wt.)	1:0.4			1:0.8			1:1.2		
2.	Formation Temperature, °C	130	150	170	130	150	170	130	150	170
3.	BET Surface area (m ² /g)	354	397	412	402	435	454	487	595	597
4.	Porosity (%)	40	41	43	42	43	43	45	46	47
5.	Pore volume (ml/g)	.193	.197	.20	.198	.20	.209	.211	.218	.219
6.	Pore Dia (Å)	4.8	4.9	5.1	4.9	5.3	5.3	5.6	6.3	6.3

Table 5.2 Physical properties of fly ash treated with lithium hydroxide

Sl No	Properties	Fly ash + 3M LiOH.H ₂ O			Fly ash + 2M LiOH.H ₂ O			Fly ash + 3M LiOH.H ₂ O		
1.	Fly ash :Alkali (wt.)	1:0.4			1:0.8			1:1.2		
2.	Formation Temperature, °C	60	90	120	60	90	120	60	90	120
3.	BET Surface area (m ² /g)	467	487	498	478	497	531	554	678	682
4.	Porosity (%)	47	48	48	49	49	50	51	51	53
5.	Pore volume (ml/g)	.201	.204	.205	.207	.209	.210	.212	.293	.291
6.	Pore Dia (A ⁰)	5.2	5.4	5.4	5.7	5.9	6.1	6.2	7.8	7.8

It was clear that fly ash treated with 3M NaOH at temperature 150 °C showed suitable conditions to remove SO₂ (BET surface area 595 m²/g , pore volume 0.218 ml/g and pore dia. 6.3 A⁰), also fly ash treated with 3M LiOH.H₂O at temperature 90 °C showed suitable conditions to remove SO₂ (BET surface area 678 m²/g , pore volume 0.293 ml/g and pore dia. 7.8 A⁰).

It was also clear that pore diameter was more in the case of Li-Zeolite, which would remove SO₂ more effectively. These results are similar as suggested in literature that if the size of cation is reduced it will give more pore volume and larger pore diameter.

(Bareer, R.M.,1982).

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Table 5.2 Physical properties of fly ash treated with lithium hydroxide

Sl No	Properties	Fly ash + 3M LiOH.H ₂ O			Fly ash + 2M LiOH.H ₂ O			Fly ash + 3M LiOH.H ₂ O		
1.	Fly ash :Alkali (wt.)	1:0.4			1:0.8			1:1.2		
2.	Formation Temperature, °C	60	90	120	60	90	120	60	90	120
3.	BET Surface area (m ² /g)	467	487	498	478	497	531	554	678	682
4.	Porosity (%)	47	48	48	49	49	50	51	51	53
5.	Pore volume (ml/g)	.201	.204	.205	.207	.209	.210	.212	.293	.291
6.	Pore Dia (A ⁰)	5.2	5.4	5.4	5.7	5.9	6.1	6.2	7.8	7.8

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(Bareer, R.M.,1982).

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5.2 Results of X-RAY Diffraction and Scanning Electron Microscopy

The result of XRD analysis for fly ash is shown in Figure 5.1 X-ray diffraction pattern of the fly ash revealed that they were composed mainly of silica rich glassy phase ($2\theta \sim 24-26^\circ$) with minor amounts of mullite and quartz. According to JCPDS file, XRD patterns obtained for fly ash treated with 3M NaOH at 150°C resulted in the formation of zeolite analcime- $\text{Na}(\text{Si}_2\text{Al})\text{O}_6 \cdot \text{H}_2\text{O}$ (Figure 5.2) and fly ash treated with 3M LiOH. H_2O at 90°C resulted in the formation of crystalline zeolite LTA- $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ (Figure. 5.3) . Tables E.1, E.2 and E.3 present the XRD data for fly ash, synthesized Na-Z and synthesized Li-Z, respectively. (Appendix E)

These results are similar to those found in the literature (Bareer, R.M, 1982).

Morphological observations of synthetic zeolites were performed using scanning electron microscope. Figure 5.4 represents SEM photomicrograph of fly ash treated with 3M NaOH at different temperature $130, 150, 170^\circ\text{C}$ and figure 5.5 represents SEM photomicrograph of fly ash treated with 3M LiOH. H_2O at different temperature $60, 90$ and 120°C . Figure 5.5 clearly indicates that zeolitization occurred at temperature 150°C in case of fly ash treated with 3M NaOH and at 90°C in case of fly ash treated with LiOH. H_2O . There was no significant change in zeolitization on further increase in temperature. Comparison of the physical properties presented in the table 5.1 and table 5.2 also supports the same.

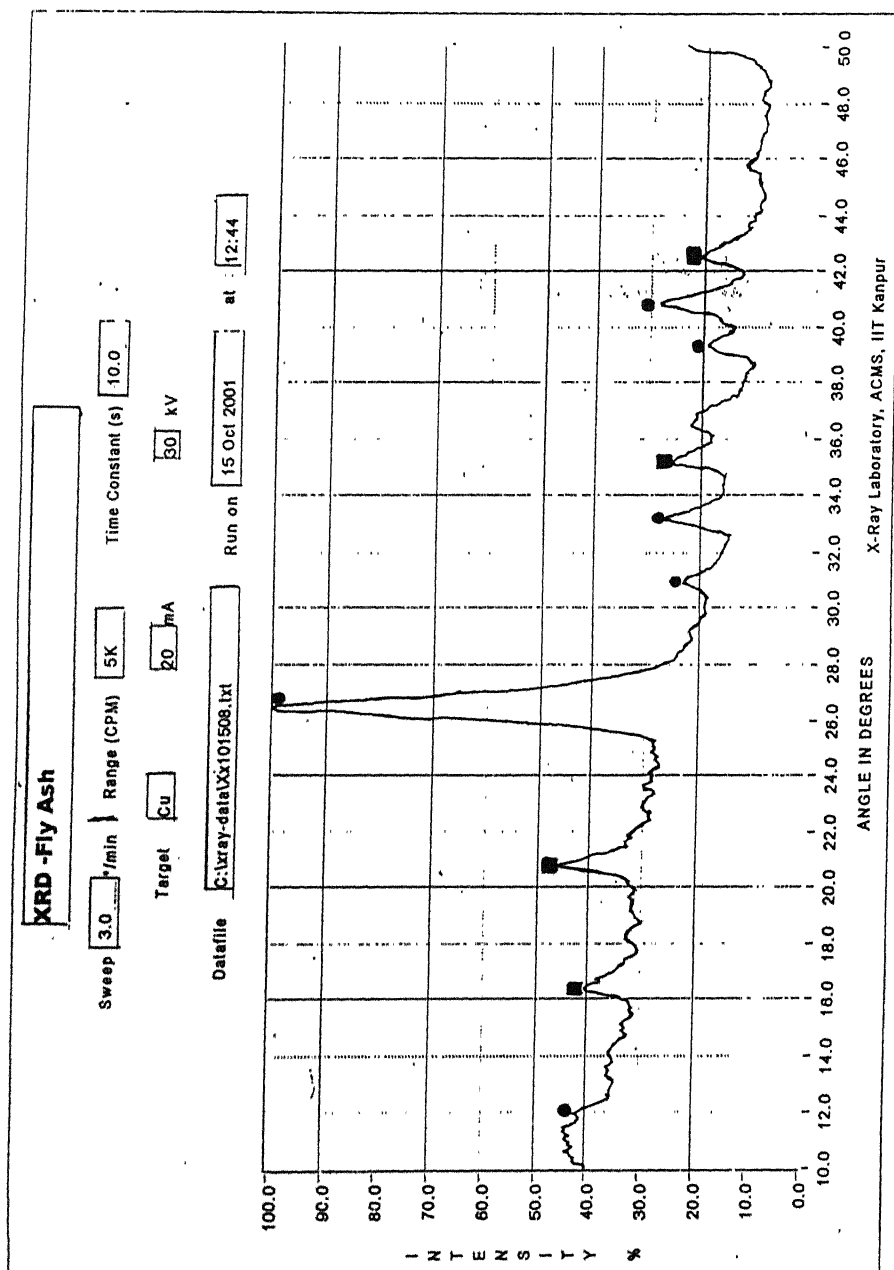


Figure 5.1 XRD of fly ash

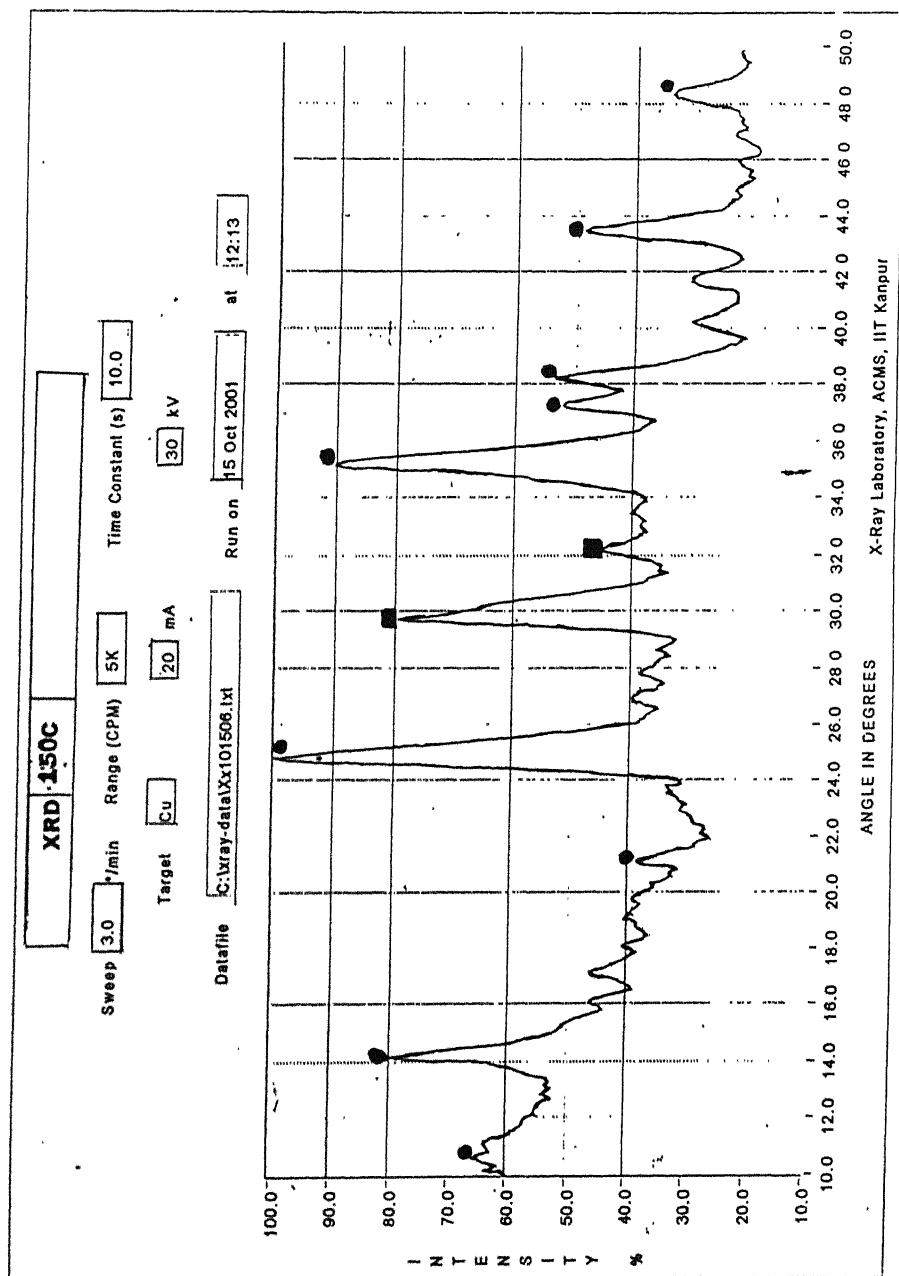


Figure 5.2 XRD of fly ash treated with 3M sodium hydroxide

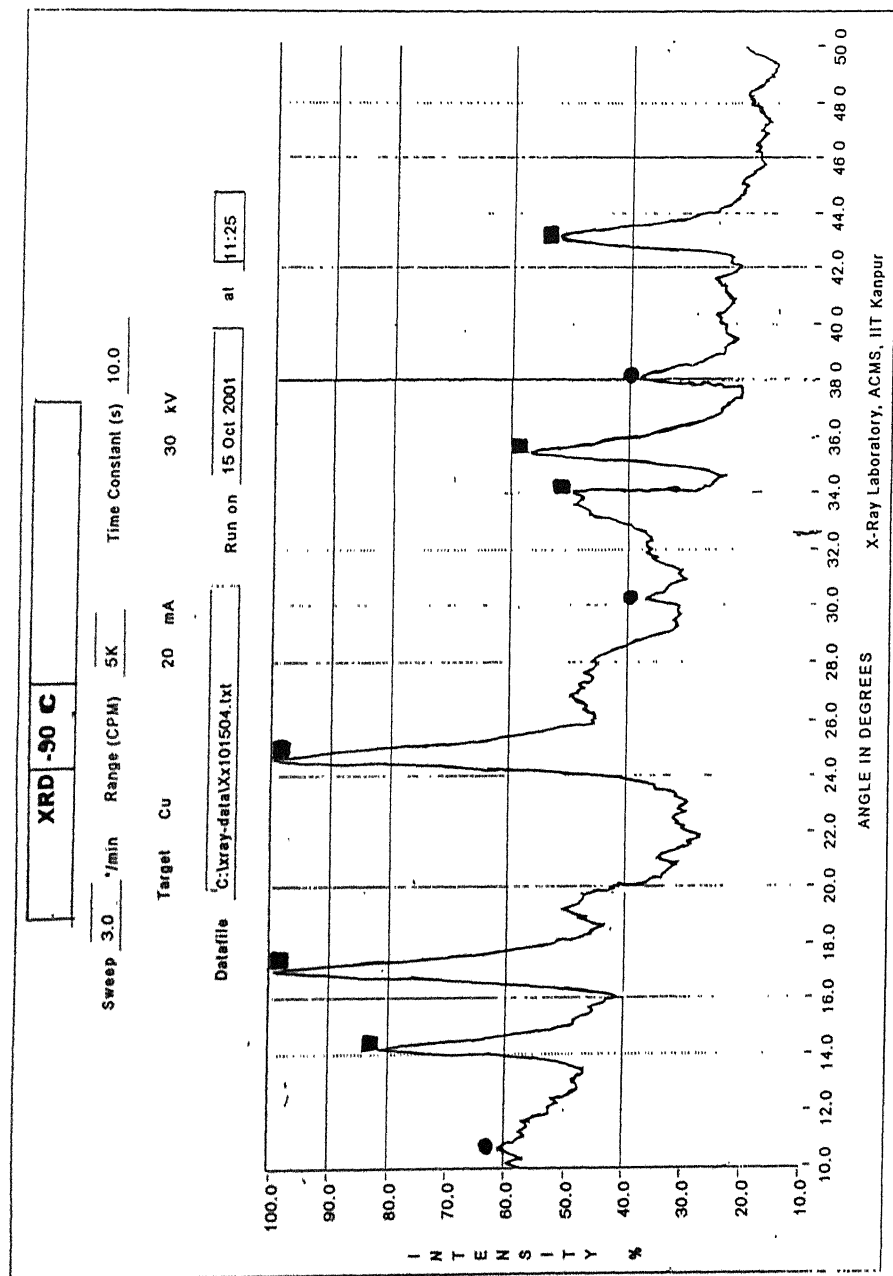


Figure 5.3 XRD of fly ash treated with 3M Lithium hydroxide

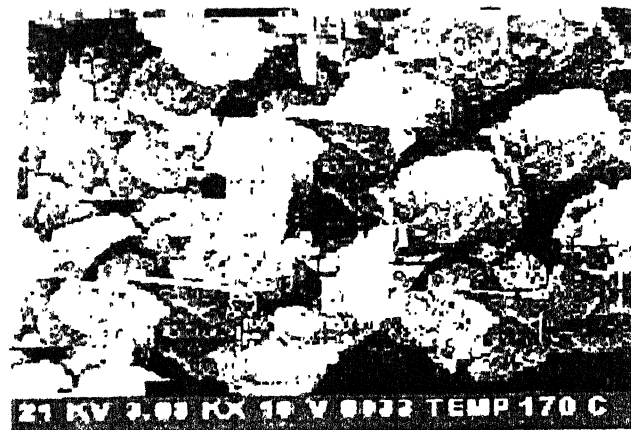
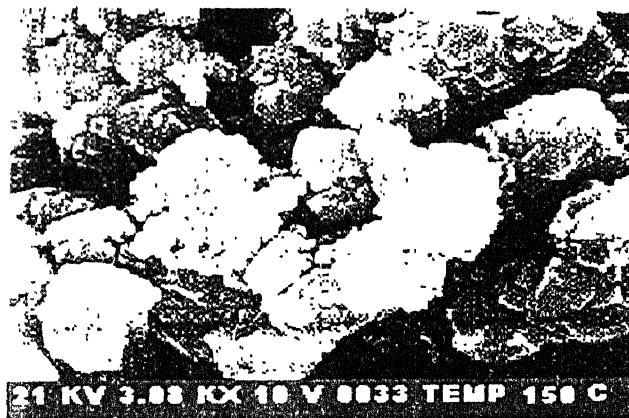
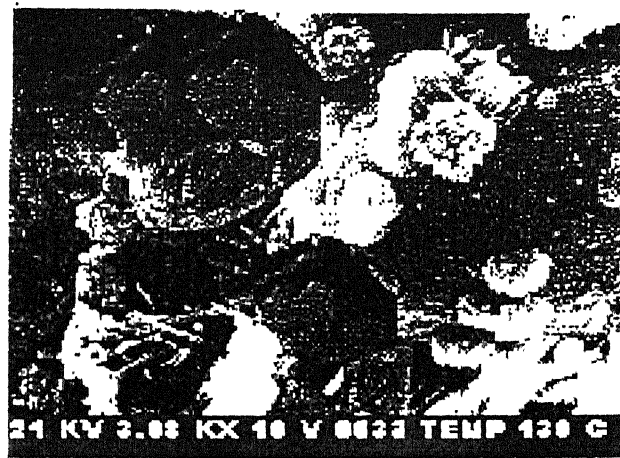


Figure 5.4 SEM images of fly ash treated with NaOH

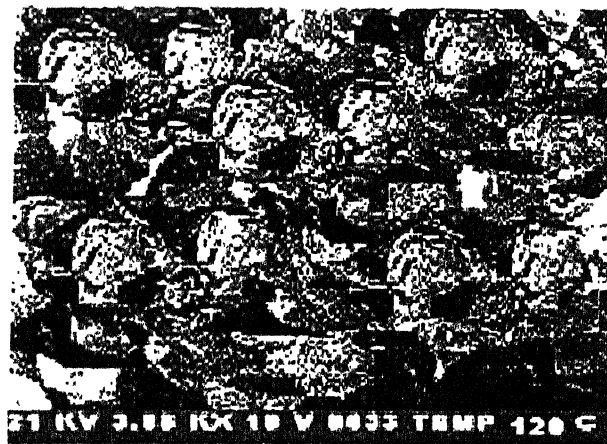
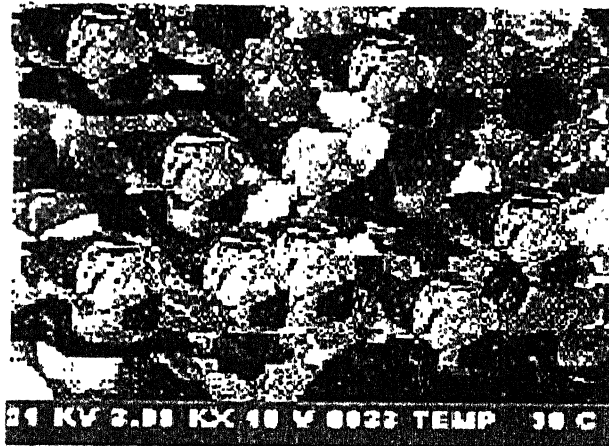
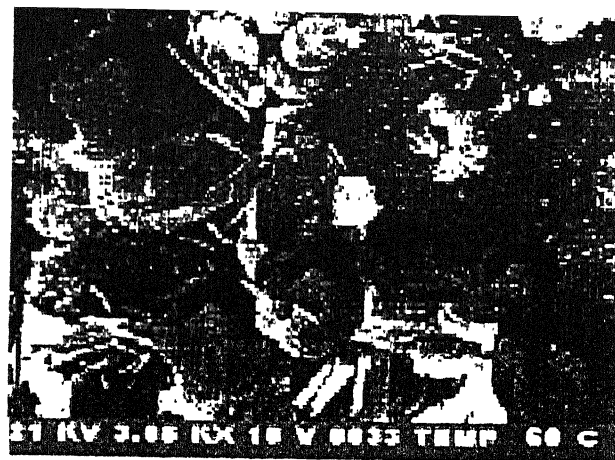


Figure 5.5 SEM images of fly ash treated with $\text{LiOH} \cdot \text{H}_2\text{O}$

On the basis of results of physical properties analysis , XRD and SEM of different samples of fly ash treated with alkali hydroxide, it is clear that zeolite analcime- $(\text{Na}(\text{Si}_2\text{Al})\text{O}_6 \cdot \text{H}_2\text{O})$ was synthesized from fly ash treated at 150°C with 3M sodium hydroxide and zeolite LT-A $(\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O})$ was synthesized from fly ash treated at 90°C temperature with 3M monohydrous lithium hydroxide. Table 5.3 represents the properties of synthesized zeolite to be used for removal of sulphur dioxide

Table 5.3 Properties of synthesized zeolites used for removal of sulphur dioxide

Sl No	Properties	Na-Zeolite (Fly ash +3M NaOH)	Li-Zeolite (Fly ash +3M LiOH.H ₂ O)
1.	Temperature	150°C	90°C
2	BET Surface area (m^2/g)	595	678
3.	Porosity (%)	48-49	53-55
4.	Pore volume (ml/g)	0.218	0.293
5.	Pore Dia (\AA)	6.3	7.8

5.3 Breakthrough curve for Sulphur Dioxide

Cleaned and oven dried sand (105°C) was used in reactor bed (maintained at 25°C) and feed gas was passed through reactor. When out let concentration became same as inlet concentration, sand was removed and the mixture of synthesized zeolite and same sand was used in ratio 1:10(by weight). Readings were taken at different times. On the basis

of above experimental study outlet concentration Vs time curves were generated for sulphur dioxide.

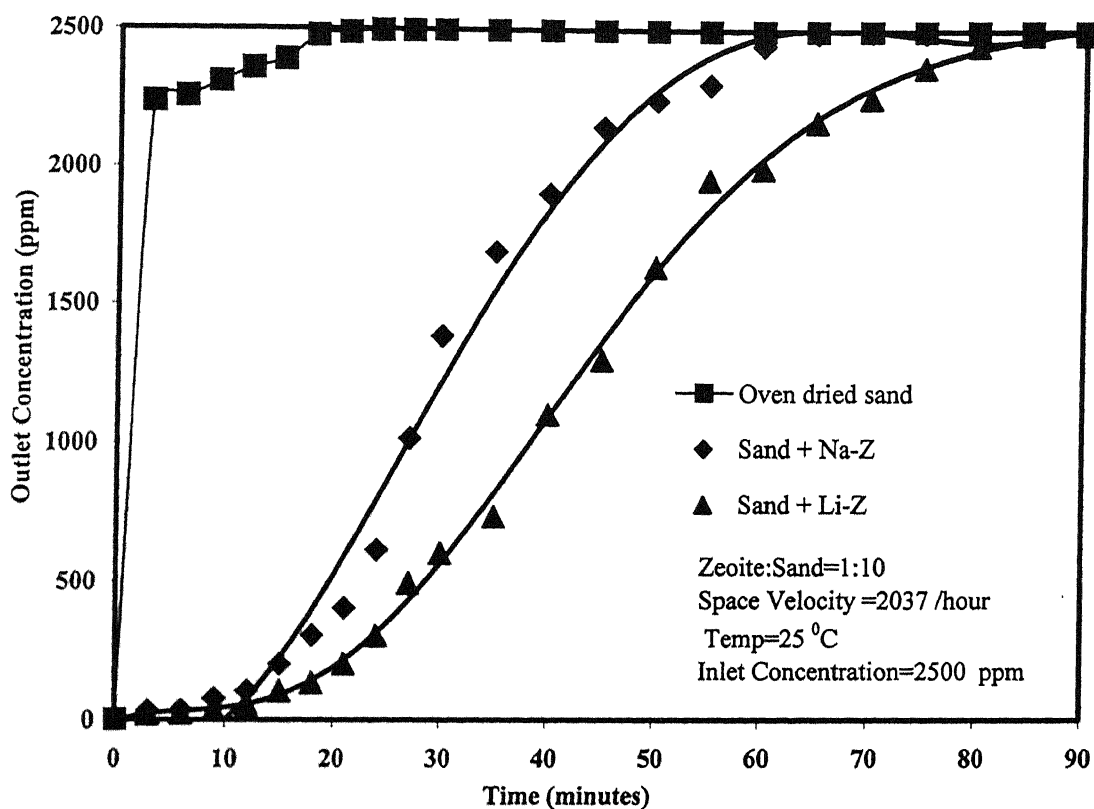


Figure 5.6 Breakthrough curve for sulphur dioxide

Fig. 5.6 represents that the removal of sulphur dioxide was more in the case of synthesized Li-Zeolite than that of synthesized Na-zeolite. It was due to more surface area and larger pore diameter. Exhaustion time was also more in the case of synthesized Li-zeolite (85 minutes) in comparison to exhaustion time of synthesized Na-Zeolite (60 minutes). Table 5.4 represents the comparison of percentage removal of sulphur dioxide. Sample calculation for calculating removal efficiency is given in Appendix-D

Table 5.4 Performance of synthesized zeolites

Sl No	Synthesized Zeolite	Temp (°C)	Inlet concentration (ppm)	Percentage removal
1	Na-Zeolite	25	2500	63 %
2.	Li-Zeolite	25	2500	74.3 %

Experimental data showed that SO₂ removal efficiency of synthesized Li-zeolite is much more than of synthesized Na-zeolite. It supports our prediction that synthesized Li-Zeolite may serve well than synthesized Na-Zeolite for removal of sulphur dioxide.

5.4 Effect of Inlet concentration on Removal of Sulphur Dioxide

Experiments were conducted at space velocity of 2037 hour⁻¹ and 25 °C through the packed bed of zeolite dispersed in sand with different inlet sulphur dioxide concentrations as 500,1000,2000 and 2500 ppm. Which is the range of sulphur dioxide emissions for most of coal combustion in field applications (Offen.et.al, 1987) Fig. 5.7 and 5.8 show the break through curves for sulphur dioxide at various inlet concentrations for both types of synthesized zeolites. Table 5.4 shows the removal efficiencies of zeolites at different inlet concentration of sulphur dioxide.

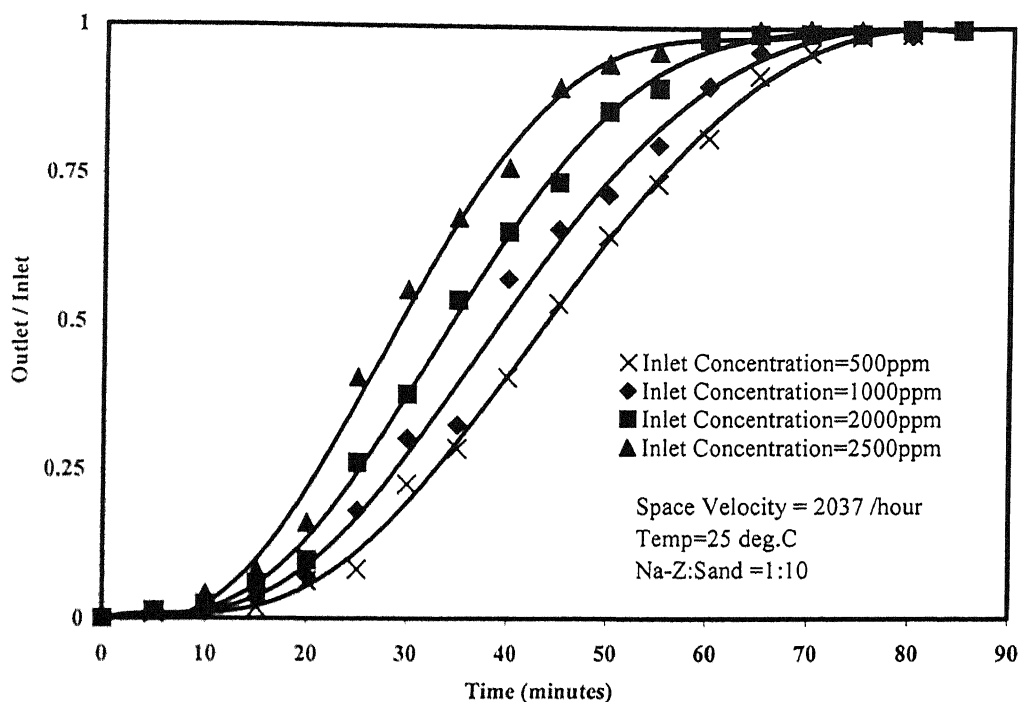


Figure 5.7 Effect of inlet concentration on sulphur dioxide removal by Na-Zeolite

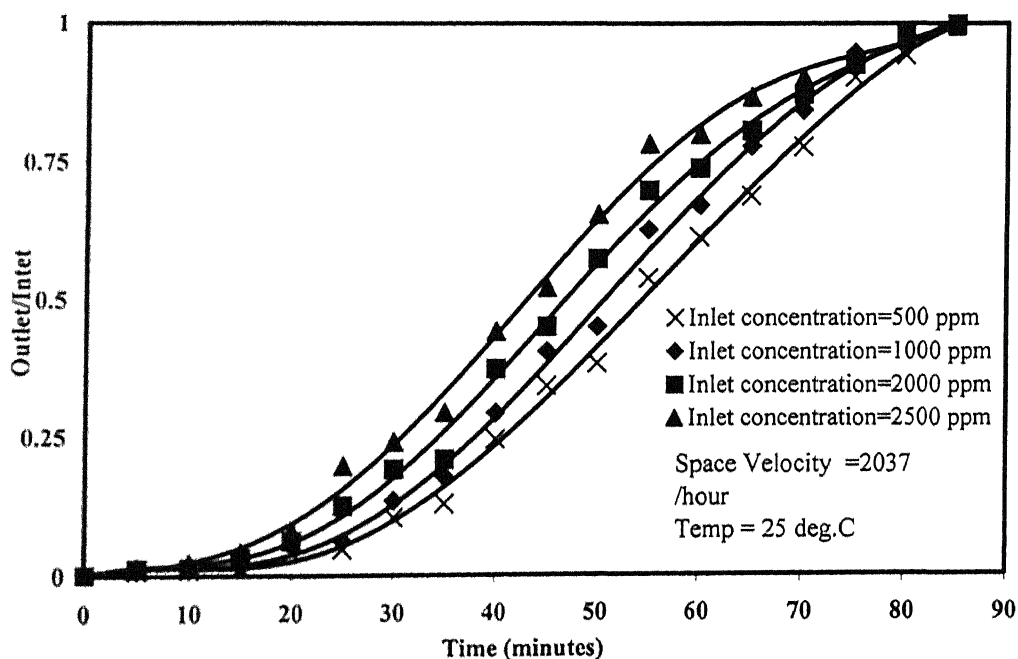


Figure 5.8 Effect of inlet concentration on sulphur dioxide removal by Li-Zeolite

Table 5.5 Effect of inlet concentration on removal of sulphur dioxide

Sl No	Synthesized Zeolite	Temp ($^{\circ}\text{C}$)	Inlet Concentration (ppm)	Percentage Removal (%)
1	Na-Zeolite	25	500	78
			1000	77
			2000	74
			2500	63
2.	Li-Zeolite	25	500	83.129
			1000	81.26
			2000	77.39
			2500	74.3

Above experiment indicates that, due to increase in the inlet sulphur dioxide concentration, the initial breakthrough of sulphur dioxide occurred quickly because that at higher concentration more active surface come in contact sooner, resulting rapid removal of sulphur dioxide. It was noted that removal efficiency was increased with the decrease in inlet concentration. This was due to increase in exhaustion time.

5.5 Effect of Temperature on Removal of Sulphur Dioxide

Experiments were conducted at various temperatures 25°C , 100°C , 150°C , 175°C and 200°C for both type of synthesized zeolite (Na-Zeolite and Li-Zeolite) at inlet gas concentration of 2500 ppm and space velocity 2037 hour^{-1} . Different breakthrough curves are presented in figure 5.9 and figure 5.10.

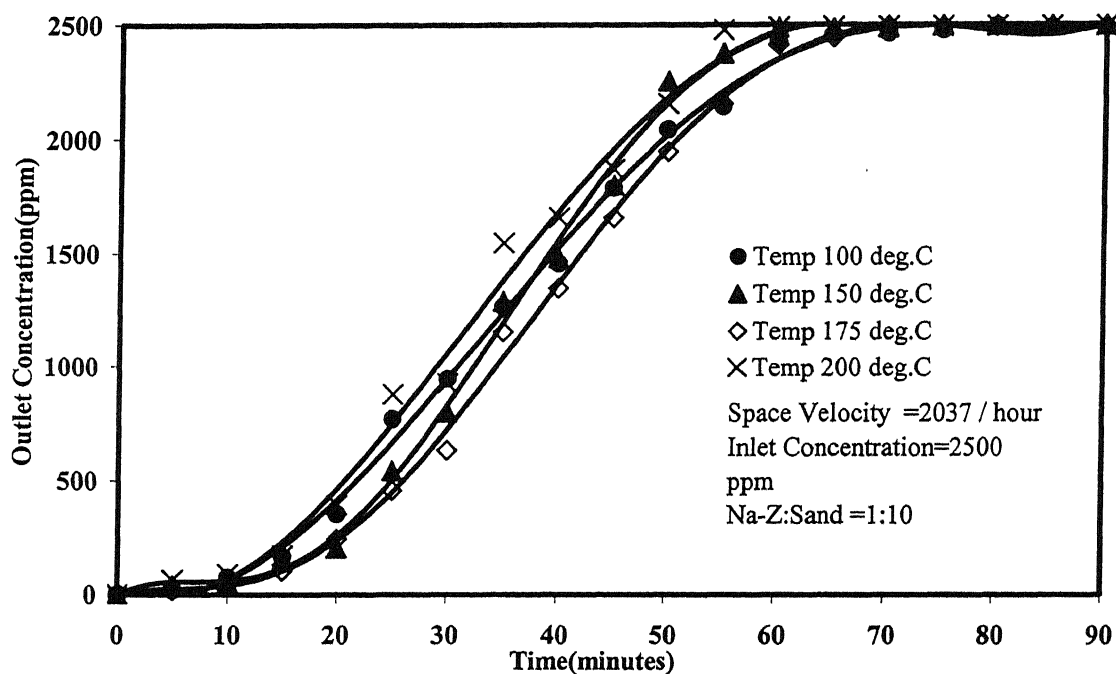


Figure 5.9 Effect of temperature on removal of sulphur dioxide by Na-zeolite

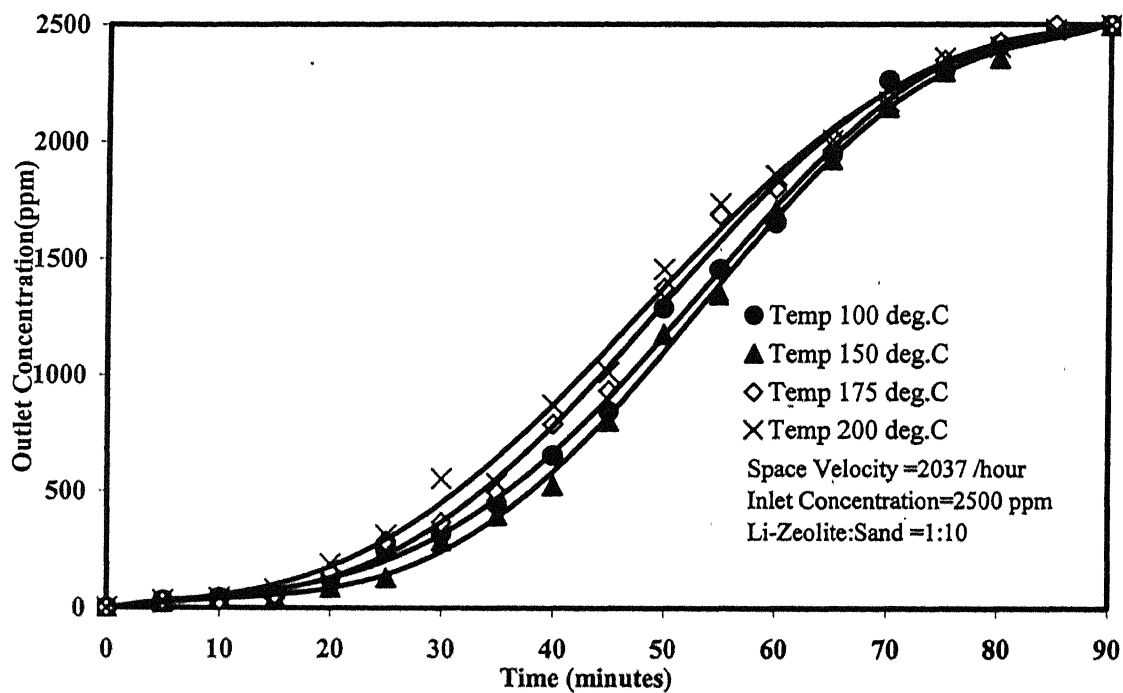


Figure 5.10 Effect of temperature on removal of Sulphur Dioxide by Li-zeolite

The removal of sulphur dioxide increased with increase in temperature up to certain extent and then declined on further increase in temperature, such behaviour indicated that within the range of study, there would be one optimum temperature at which the removal of sulphur dioxide would be maximum. (175 °C for synthesized Na-Zeolite and 150 °C for synthesized Li-Zeolite). It was also noted that due to increase in reaction rate initial breakthrough curve occurred quicker at higher temperature but the exhaustion time was more or less same. Sulphur dioxide removal efficiencies were also calculated for different operating temperature as shown in Table 5.5.

Table 5.6 Effect of temperature on removal of sulphur dioxide

Sl No	Synthesized Zeolite	Temp (°C)	Inlet Concentration (ppm)	Percentage Removal (%)
1	Na-zeolite	100	2500	70.3
		150	2500	72.34
		175	2500	78.16
		200	2500	69.14
2.	Li-Zeolite	100	2500	78.94
		150	2500	83.58
		175	2500	81.265
		200	2500	76.20

On the basis of above study it is clear that removal of Sulphur dioxide is also dependent on operating temperature and there is one optimum temperature after which change in crystal orientation of zeolite takes place resulting in less removal of sulphur dioxide.

5.6 Regeneration of Synthesized Zeolites

Regeneration was carried out by heating synthesized Na-Zeolite and synthesized Li-Zeolite in absence of oxygen. Outlet gas composition was continuously checked to ensure the presence of sulphur dioxide in out-coming gas mixture. In case of synthesized Li-Zeolite, at 650 °C, fair proportion of sulphur dioxide was observed in outlet gas mixture while sulphur dioxide could not be traced out in the case synthesized Na-Zeolite with in the range of temperature studied. Figure 5.11 shows the performance of regenerated synthesized zeolites.

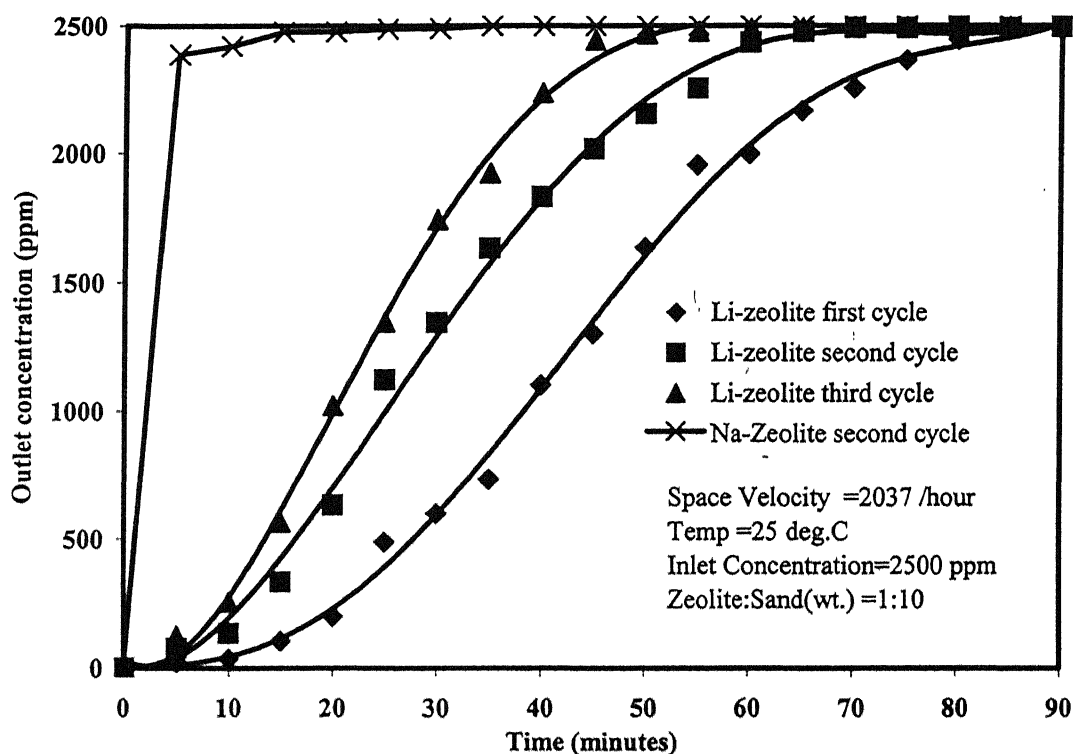


Figure 5.11. Breakthrough curve for sulphur dioxide removal by regenerated synthesized zeolites

Figure 5.11 indicates that for synthesized Na-Zeolite, regeneration did not occur or would take place at very high temperature but regeneration was possible in case of Li-Zeolite. One possible cause of such result may be that reaction of sulphur dioxide with synthesized Na-Zeolite might have formed some stable compounds, which were not easy to break and compounds formed by Li-Zeolite were easy to break with in the temperature range studied.

After regeneration removal efficiency was calculated according to the sample calculation present in the Appendix-D. On the basis of above study it was clear that Li-Zeolite could be regenerated but after third cycle only 42 % sulphur dioxide could be removed.

Analysis of Compounds, produced after removal of sulphur dioxide, could also be done to have clear idea about the type of removal and properties of compounds, which could provide sufficient information about the failure of synthesized Na-Zeolite regeneration with in the temperature range studied.

6. Conclusions

In the present experimental work removal of sulphur dioxide by the synthesized zeolites was examined.

- Treatment of fly ash with alkali hydroxide resulted in synthesis of zeolite. It was noted that Li-Zeolite was synthesized at lower temperature than Na-Zeolite and had more pore diameter and surface area than that of synthesized Na-Zeolite, which would enhance the sulphur dioxide removal.
- In a packed bed of zeolite dispersed in sand, at 25 °C and 2500 inlet sulphur dioxide concentration synthesized Na-Zeolite removed 63 % sulphur dioxide and synthesized Li-Zeolite removed 74.3 %. This supports our prediction that synthesized Li-Zeolite may remove more sulphur dioxide than removed by synthesized Na-Zeolite.
- Study on the effects of various operating conditions showed that removal efficiency was increased with the decrease in inlet concentration and in the range of 25-200 °C there was an optimum temperature at which the removal of sulphur dioxide was maximum (175 °C for Na-Zeolite and 150 °C for Li-Zeolite).
- Regeneration of synthesized Li-Zeolite was possible at 650 °C in absence of oxygen but synthesized Na-Zeolite could not be regenerated within the range of

temperature studied. After the third cycle sulphur dioxide removal efficiency of synthesized Li-Zeolite was reduced up to 42 % .

- One other unfortunate result is that synthesized zeolites were still very fine. If this synthesized zeolite material is to have a commercial use, it would have to be palletized to make handling more convenient.

XRD Analysis of products after removal of sulphur dioxide could also be done to have in-depth idea about the removal process and type of compound formed, which could provide sufficient information about the failure of regeneration of synthesized sodium zeolite.

Present work indicates that zeolite synthesized from fly ash and alkali hydroxide may be used as sulphur dioxide removal medium and synthesized Li-Zeolite has better removal efficiency than that of synthesized Na-Zeolite. Regeneration is also possible for synthesized Li-Zeolite. So it can be concluded that Li-Zeolite may be better option than Na-Zeolite to be used to remove sulphur dioxide in plants such as sulphuric acid and ore extraction plants.

7. Suggestions for Future Work

The following points are suggested for carrying out further work.

- Medium was highly basic so acidic gases other than sulphur dioxide may also be examined for removal. Effect of concentration of carbon dioxide on removal of sulphur dioxide may also be studied.
- Mechanism behind the removal of sulphur dioxide and regeneration of zeolite may be studied for enhancing removal and regeneration.
- Effect of change in Al/Si ratio of fly ash on removal of sulphur dioxide may also be studied by modifying fly ash with the use of some additives such as aluminate compounds .

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Appendix –A

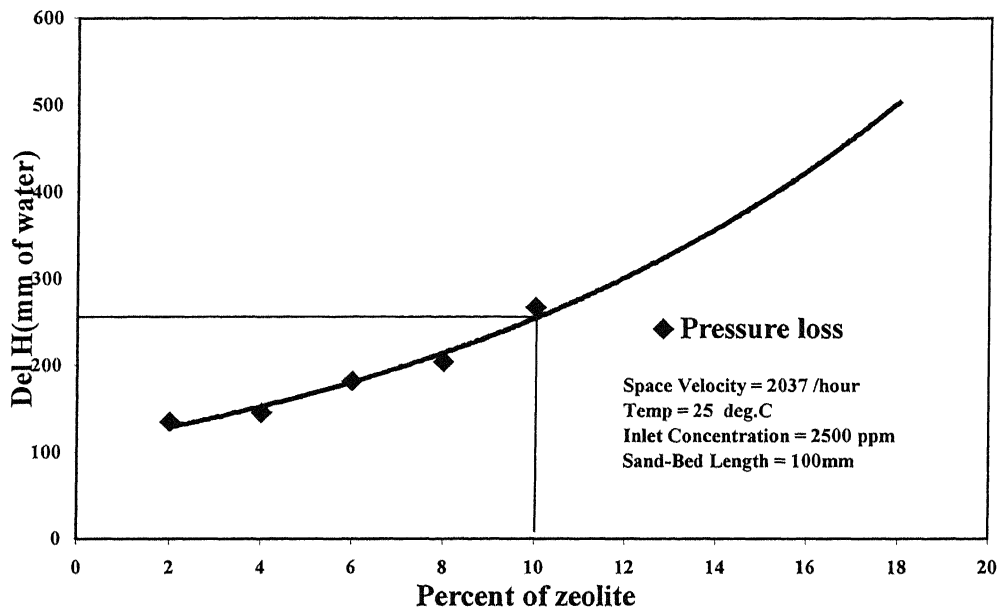


Figure A.1 Pressure loss Vs percent of synthesized zeolite dispersed in sand-bed reactor

Table A.1 Pressure loss Vs percent of synthesized zeolite dispersed in sand-bed reactor

Sl No.	Percent zeolite (weight) in sand-bed *	Pressure loss (mm of water)
1	2	135
2	4	145
3	6	182
4	8	204
5	10	260
6	12	300
7	15	374

* Locally available sand passing through 1.0 mm and retained on 600 μ m IS test sieve.

Appendix – B

Sand Bed as Plug Flow Model

The intensity of dispersion was estimated using method of Levenspiel(1988).The Reynold (Re), Schemidt(Sc) numbers were found as shown below

D_p = particle diameter, cm

ρ = gas density, gm /cm³

u = gas velocity, cm /s

μ = gas viscosity, gm /cm/s

D' = Sulphur Dioxide molecular diffusion coefficient, cm² /s

L = height of sand bed reactor, cm

$Re = (D_p \times u \times \rho) / \mu = 6 \times 10^{-2} \times 5.65 \times 1 \times 10^{-3} \div 1.9 \times 10^{-4} = 1.78$

$Sc = \mu / \rho D'$
 $= 1.9 \times 10^{-4} / (1 \times 10^{-3} \times 0.156) = 1.2$

From fig. 18 in levenspiel corresponding to $Re = 1.78$ and $Sc = 1.2$

$(D \times \xi) / (u \times d_p) = 0.325$

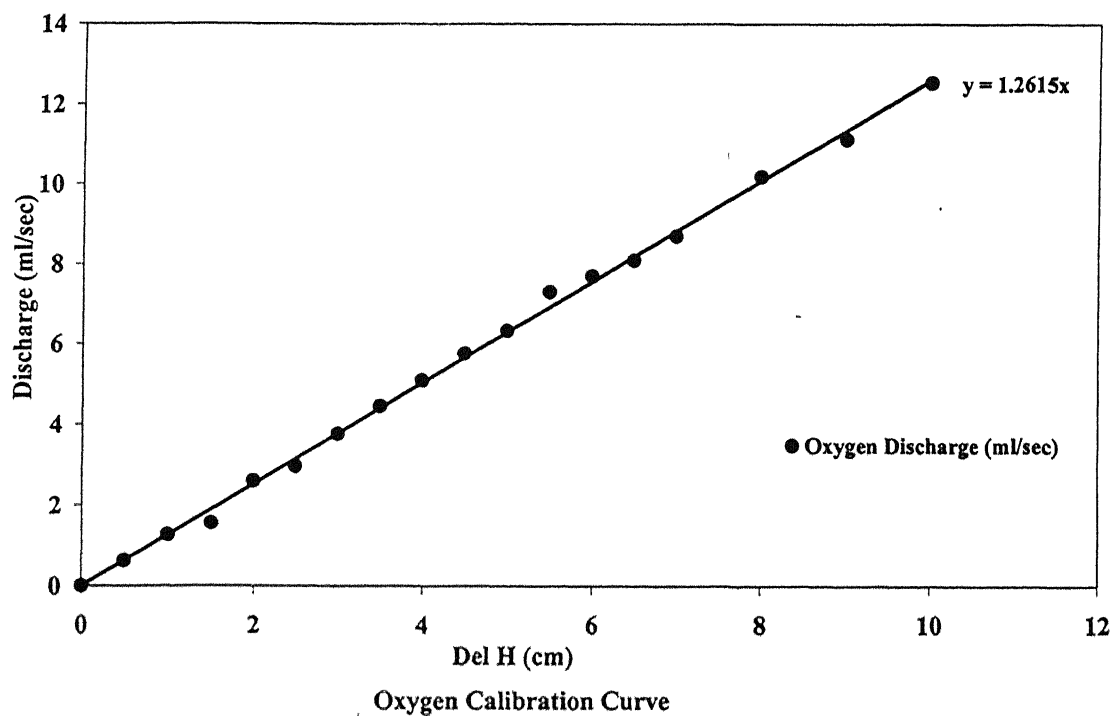
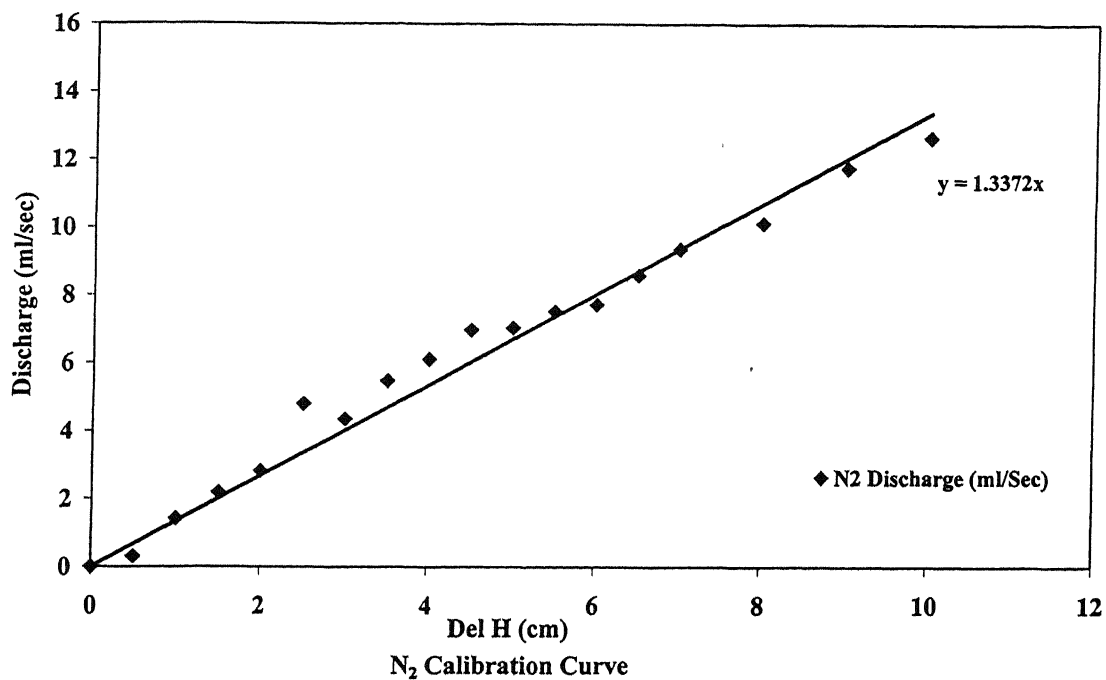
$D = 0.325 \times 5.65 \times 6 \times 10^{-2} \div 0.49 = .2248$

dispersion number = $D / u \times L$

$= .0039$

this low dispersion number suggests that the effect of mixed flow probably can be disregarded and that a plug flow model was a reasonable assumption.

Appendix -C



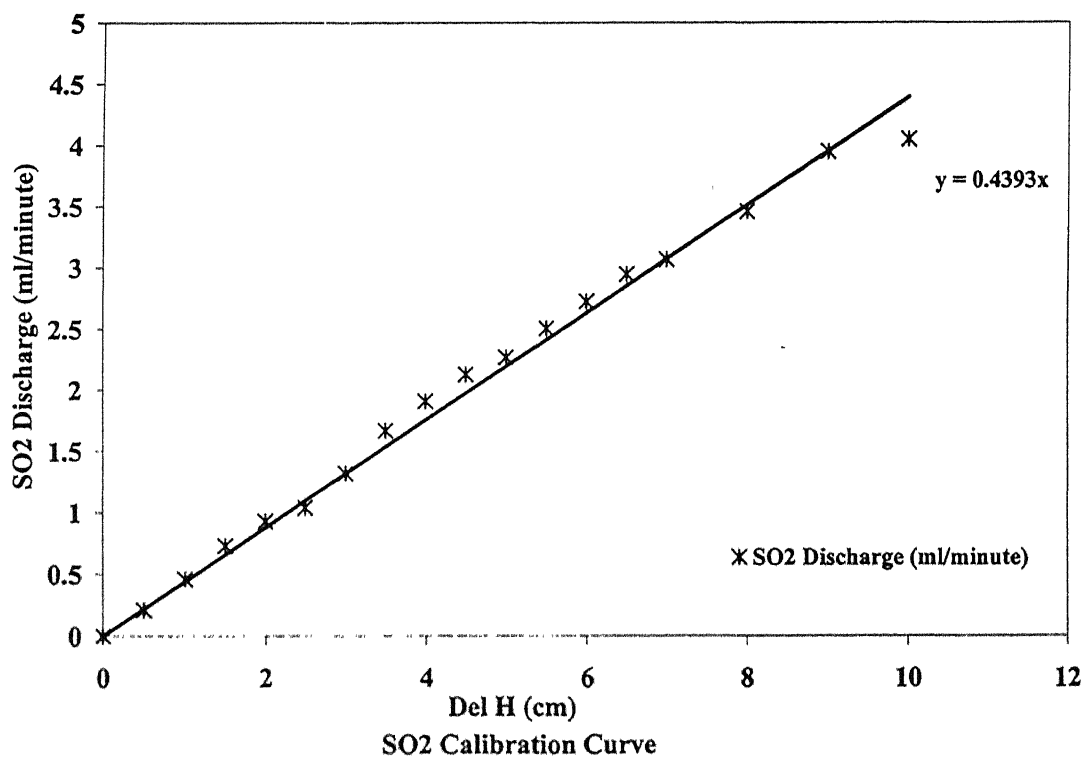
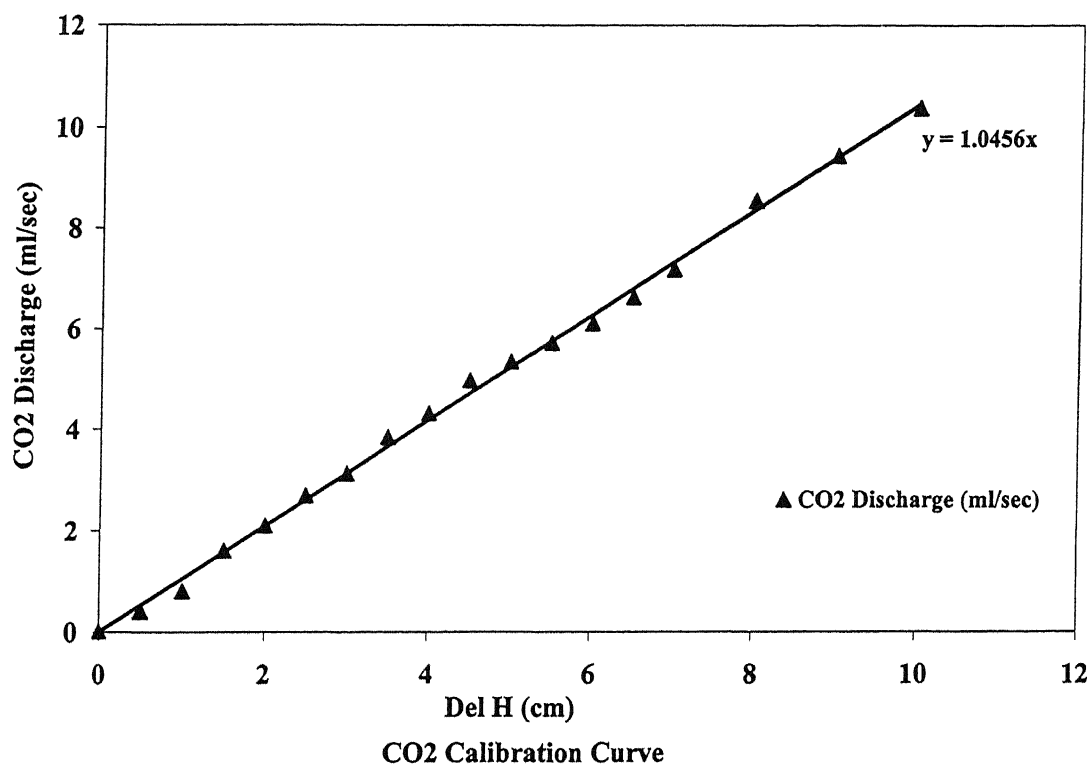


Figure C.1 Calibration curves for gases

Appendix –D

Calculation for percent sulphur dioxide removal.

The following calculations are based on the breakthrough curve for the inlet 'Sulphur Dioxide' concentration of 2500 ppm space velocity 2037 per hour and 25 °C temperature as shown in figure 5.6

Percentage removal in case of Na-Zeolite

The total amount sulphur dioxide removed, during the test run can be obtained by calculating the area above the recorded breakthrough curve.

It was known that, 1 ppm of sulphur dioxide = $2617.6 \mu\text{g} / \text{m}^3$ (at 25 °C)

SO_2 supplied during experiment = $2500 \times 2617.6 \times 10 \times 10^{-6} \times 60 \times 60 = 0.2355 \text{ gm}$

Value of one square on the graph = $350 \times 2617.6 \times 10 \times 10^{-6} \times 5 \times 60 = 2748.48 \mu\text{g}$

Total sulphur dioxide removed = $54 \times 2748.48 = 0.148 \text{ gm}$

Percentage removal = $(0.1483 \div 0.2355) \times 100 = 63 \%$

for the present work 5 gm of synthesized zeolite was used with 50 gm of sand

SO_2 removed per g of zeolite = $0.148 \div 5 = 29.6 \text{ mg sulphur dioxide} / \text{g of zeolite}$

Percentage removal in case of Li-Zeolite

sulphur dioxide supplied = $2500 \times 2617.6 \times 10 \times 10^{-6} \times 90 \times 60 = 0.354 \text{ gm}$

total sulphur dioxide removed = $96 \times 2748.48 = 0.263 \text{ gm}$

percentage removal = 74.3 %

SO_2 removed per g of zeolite = $0.263 \div 5 = 52.6 \text{ mg of sulphur dioxide} / \text{g of zeolite}$

Appendix E

Table E.1 XRD Data of Fly Ash

Intensity %	Angle $^{\circ}$	d A $^{\circ}$
40.90	16.43	5.396030
32.65	18.31	4.846236
32.30	19.69	4.508524
46.46	20.83	4.264860
28.85	22.76	3.907647
29.85	23.00	3.866208
30.06	23.65	3.762551
29.08	24.09	3.694051
28.64	25.18	3.536878
99.90	26.51	3.361751
21.62	29.09	3.070167
19.06	30.12	2.966667
22.97	30.96	2.888025
26.39	33.24	2.695424
25.40	35.27	2.544941
21.96	36.55	2.458379
18.9	39.37	2.288648
28.13	40.85	2.208911
20.88	42.53	2.125420

Table E.2 XRD Data of Fly Ash Treated with 3M Sodium Hydroxide at 150 °C

Intensity %	Angle °	d Å
77.69	14.22	6.227219
45.89	16.09	5.508979
46.29	17.12	5.179422
40.57	18.05	4.913807
39.58	19.13	4.638744
37.71	21.10	4.211120
30.90	22.96	3.871991
32.24	23.60	3.769667
100.00	24.78	3.593000
40.10	26.94	3.309563
38.72	27.87	3.200874
35.66	28.66	3.114891
79.46	29.79	2.999320
45.53	32.19	2.780452
39.62	33.57	2.669654
89.83	35.24	2.546909
52.00	37.30	2.410699
53.04	38.18	2.356910
30.27	40.25	2.240772

Table E.3 XRD Data of Fly Ash Treated with 3M Lithium Hydroxide at 90 °C

Intensity %	Angle °	d Å⁰
81.79	14.22	6.230299
98.59	16.67	5.382072
37.44	17.40	5.096061
37.89	18.14	4.891088
42.23	19.26	4.607311
40.82	19.85	4.472106
98.29	24.66	3.610612
49.71	26.86	3.318920
47.63	27.65	3.226523
36.87	29.29	2.950337
49.32	30.09	2.665137
57.36	35.63	2.567187
38.61	38.04	2.365573
52.19	43.14	2.097084